

# **Properties of Cd and Zn Partial Electrolyte Treated CIGS Solar Cells**

## **Preprint**

K. Ramanathan, F.S. Hasoon, S. Smith, A. Mascarenhas,  
H. Al-Thani, J. Alleman, H.S. Ullal, and J. Keane  
*National Renewable Energy Laboratory*

P.K. Johnson and J.R. Sites  
*Physics Department, Colorado State University*

*To be presented at the 29<sup>th</sup> IEEE PV Specialists Conference  
New Orleans, Louisiana  
May 20-24, 2002*



**NREL**

**National Renewable Energy Laboratory**

1617 Cole Boulevard  
Golden, Colorado 80401-3393

NREL is a U.S. Department of Energy Laboratory  
Operated by Midwest Research Institute • Battelle • Bechtel

Contract No. DE-AC36-99-GO10337

## NOTICE

The submitted manuscript has been offered by an employee of the Midwest Research Institute (MRI), a contractor of the US Government under Contract No. DE-AC36-99GO10337. Accordingly, the US Government and MRI retain a nonexclusive royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for US Government purposes.

This report was prepared as an account of work sponsored by an agency of the United States government. Neither the United States government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States government or any agency thereof.

Available electronically at <http://www.osti.gov/bridge>

Available for a processing fee to U.S. Department of Energy  
and its contractors, in paper, from:

U.S. Department of Energy  
Office of Scientific and Technical Information  
P.O. Box 62  
Oak Ridge, TN 37831-0062  
phone: 865.576.8401  
fax: 865.576.5728  
email: [reports@adonis.osti.gov](mailto:reports@adonis.osti.gov)

Available for sale to the public, in paper, from:

U.S. Department of Commerce  
National Technical Information Service  
5285 Port Royal Road  
Springfield, VA 22161  
phone: 800.553.6847  
fax: 703.605.6900  
email: [orders@ntis.fedworld.gov](mailto:orders@ntis.fedworld.gov)  
online ordering: <http://www.ntis.gov/ordering.htm>



Printed on paper containing at least 50% wastepaper, including 20% postconsumer waste

# PROPERTIES OF Cd and Zn PARTIAL ELECTROLYTE TREATED CIGS SOLAR CELLS

K. Ramanathan, F.S. Hasoon, S. Smith, A. Mascarenhas, H. Al-Thani, J. Alleman, H.S. Ullal and J. Keane  
National Renewable Energy Laboratory, 1617 Cole Boulevard, Golden CO 80401

P.K. Johnson and J.R. Sites  
Physics Department, Colorado State University, Fort Collins CO 80523

## ABSTRACT

We study the influence of Cd partial baths on the photovoltaic properties of  $\text{CuInGaSe}_2$  (CIGS) and  $\text{CuInGaSSe}_2$  (CIGSS) thin film absorbers. We find that efficient solar cells can be fabricated by this treatment, and we compare their properties with those containing CdS window layers grown by chemical bath deposition. The results suggest that Cd plays a dominant role in establishing efficient photovoltaic junctions in  $\text{CuInSe}_2$  alloys. Micron scale photoluminescence scans show non-uniformity along the length probed. Cd treatment quenches one of the luminescence transitions, which indicates a change in shallow acceptor level density. We present a model that helps to explain the evolution of photovoltaic action.

## INTRODUCTION

$\text{CuInSe}_2$  (CIS) thin films and their alloys with  $\text{CuGaSe}_2$  and  $\text{CuInS}_2$  have been the subject of study in the photovoltaic community because of their suitability for low-cost power generation. Excellent cell efficiencies are demonstrated routinely in laboratory scale devices [1], and large area modules are entering the marketplace [2]. A majority of the laboratory scale devices are fabricated from CIGS alloys deposited by co-evaporation of the elements. Large area modules are made from CIGSS absorbers derived from sputtered metal precursors and subsequent reaction with the chalcogens. The two examples provide a sharp contrast in terms of the preparation of the absorber materials. In any further analysis of the physics of the devices, one must take into account the differences in the preparation methods and the resulting absorber properties. A reasonable starting point is that the absorbers are single-phase, chalcopyrite  $\text{Cu}(\text{In,Ga})(\text{SSe})_2$  alloy thin films in which the Ga and/or S mole fractions are carefully controlled to be within tolerance limits, and the Cu composition is also controlled to avoid Cu chalcogenide impurities. In all of these materials, the junction formation is achieved by the growth of a thin CdS window layer by chemical bath deposition (CBD). CBD CdS processing produces the most efficient solar cells. However, the mechanism that forms the junction remains unclear. Historically, the CdS/CIGS interface has been treated as a "non-interacting," or abrupt junction. There are a few reports [3,4] suggesting that the interface is intermixed, or may contain distinct compounds such as  $\text{CdSe}$  or  $\text{CdIn}_2\text{Se}_4$ . The temperature of CBD growth is deceptively low, but the

chemical driving forces are powerful enough to cause dissolution of species and cause atomic movements [5]. This is also illustrated in the case of aqueous treatment of CIS in In-S solutions in which a thin  $\text{CuInS}_2$  layer is grown on the surface [6]. Compositional changes such as those mentioned above have not been adequately treated in further analysis of the junction. A more serious omission is the potential role of electrically active impurities, such as Cd or Zn, which are known to produce efficient n-type conductivity [7] in the materials of interest. We have shown previously that the CBD reaction mixture containing only Cd, or a similar bath constituted with Zn, can be used to produce efficient photovoltaic cells in  $\text{CuInSe}_2$  thin films [5]. In this report, we extend this work to high-efficiency CIGS absorbers fabricated by the three-stage process [8], and CIGSS absorbers provided by Shell Solar Industries (SSI).

## EXPERIMENTAL

CIGS thin films were grown by the three-stage process on Mo/soda lime glass substrates. The resulting absorber material was 2.5  $\mu\text{m}$  thick, and it was p-type with a hole density of  $1\text{-}3 \times 10^{16} \text{ cm}^{-3}$ . The nominal composition was  $\text{CuIn}_{0.7}\text{Ga}_{0.3}\text{Se}_2$ . The Cu concentration in the near-surface region was carefully controlled so that the overall Cu/(In+Ga) ratio is less than unity. Absorbers provided by SSI were graded CIGSS materials. CdS thin films were deposited from an aqueous solution containing 0.0015M  $\text{CdSO}_4$ , 1.5M  $\text{NH}_4\text{OH}$ , and 0.0075M thiourea. The temperature of the bath was raised from room temperature to 60°C, and the samples were held in the bath for 15 min, during which a 40 to 60 nm CdS film was deposited. Partial electrolyte treatments, designated as Cd PE and Zn PE, were performed by immersing the samples in a bath similar to the CdS deposition, but excluding thiourea. The maximum temperature during the Cd PE treatment was 80°C, and the total immersion time was 22 min. Solar cells were fabricated by depositing a two-layer ZnO film. The first layer of 80 to 100 nm was deposited from a pure ZnO target, and the second layer of 200 nm was deposited from an  $\text{Al}_2\text{O}_3$  doped target. Ni/Al contacts were evaporated on the ZnO. Current-voltage characteristics of the solar cells were measured in dark and under light simulated to correspond to AM1.5 Global spectrum. Photoluminescence (PL) was excited by a He-Ne laser and collected by a InGaAs diode array detector. The samples

were held at 4 K in a liquid-He cold finger cryostat, and the excitation level was about 120 nW.

### RESULTS AND DISCUSSION

Fig. 1 shows the light current-voltage (J-V) characteristics of three types of solar cells fabricated from NREL CIGS absorbers. Sputter deposition of ZnO directly on the CIGS (open circles) does not produce a well-behaved diode. The Cd PE treatment prior to the ZnO deposition (solid circles) results in a marked improvement, and an efficient solar cell is achieved. A comparison with

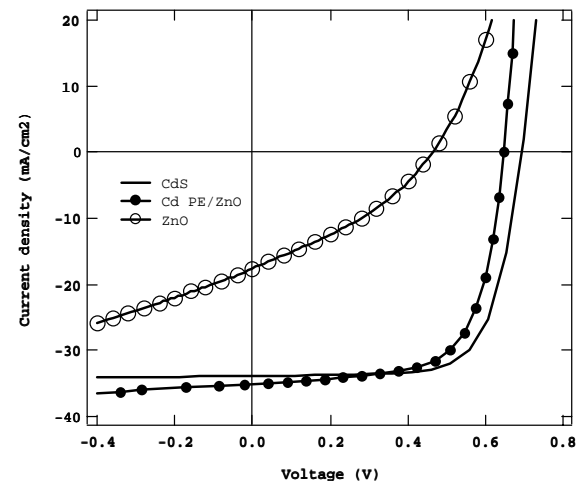


Fig. 1. Light J-V curves for solar cells fabricated on NREL CIGS absorbers.

the solar cell with a CdS window layer (solid line) demonstrates the beneficial effect of Cd in creating a strong electric field within the device.

Fig. 2 is an example of these effects in CIGSS graded absorbers prepared by SSI in a manner that has no similarity to the CIGS absorbers. The trends are similar to the CIGS case, and demonstrate that Cd is equally effective in “real-world” materials.

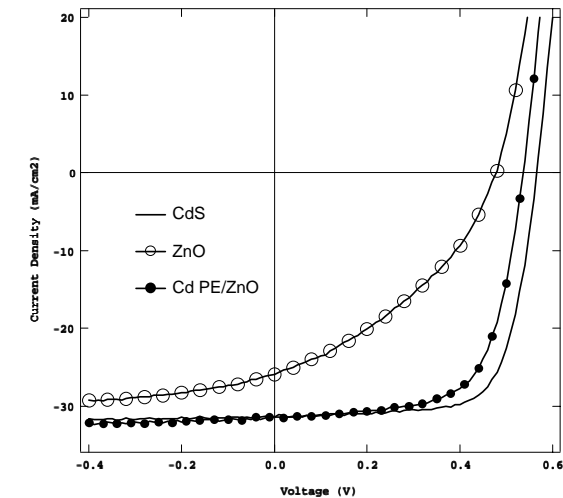


Fig. 2. Light J-V curves for a solar cells fabricated on SSI CIGSS graded absorbers.

The best solar cell made using Cd PE treatment has demonstrated a conversion efficiency of 15.7%. Another device made using Zn PE treatment produced a 14.2% solar cell. Both were characterized by NREL under standard reporting conditions. The solar cell parameters are shown in Table 1. These cells were fabricated from different absorbers with different Ga contents, and a direct comparison of the two cannot be made without taking into account the specific process details.

Table 1. Light J-V Parameters of Solar Cells Made Using Cd PE and Zn PE. Device Structure is MgF<sub>2</sub>/ZnO/CIGS.

Treatment	V <sub>oc</sub> (V)	J <sub>sc</sub> (mA/cm <sup>2</sup> )	FF	Efficiency (%)
Cd PE	0.636	34.6	0.72	15.7
Zn PE	0.558	36.3	0.70	14.2

Internal quantum efficiency of Cd PE and CdS cells fabricated on the same absorber are shown in Fig. 3. The Cd PE cell exhibits a superior collection in the short wavelengths due to the absence of absorption and collection losses related to the CdS. The long wavelength response is maximized as well. The differences in the long wavelength edge are due to the differences in the Ga content. Capacitance-voltage characteristics of the CdS and Cd PE cells were studied as a function of post-heating after the deposition of CdS or Cd PE treatment. The carrier density profiles are changed by short anneals in air at 200°C. In the Cd PE cells, we have observed a lower carrier density and, hence, a larger depletion width. This is likely the result of higher process temperature and a consequent compensation of holes by Cd donors. The red response is enhanced as a result of field assisted collection. This aspect is discussed in another paper at this conference [9].

In general, the efficiency of the Cd PE cells are lower than the CdS cells fabricated on the same absorbers. V<sub>oc</sub>’s and fill factors are lower, whereas the current density is higher. To understand the potential causes for the dif-

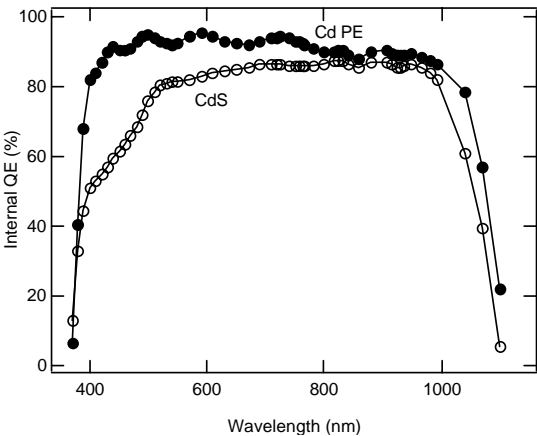


Fig. 3. Quantum efficiency of CIGS cells with CdS and Cd PE treatment.

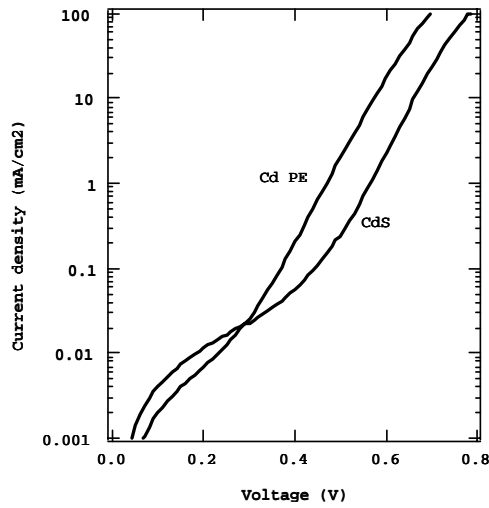


Fig. 4. Dark J-V characteristics of Cd PE and CdS solar cells.

Table 2. Diode Quality Factor, A, and Reverse Saturation Current Density,  $J_0$  ( $A/cm^2$ ), of CdS and Cd PE cells.

Type	A (dark)	$J_0$ (dark)	A (light)	$J_0$ (light)
CdS	1.7	$10^{-9}$	1.7	$10^{-8}$
Cd PE	1.9	$10^{-7}$	2.0	$10^{-7}$

ferences, we measured the J-V characteristics and these are shown in Fig. 4. An analysis of the dark and light J-V characteristics was performed, and a summary is shown in Table 2. The reverse saturation current density,  $J_0$ , of the Cd PE cell in the dark is two orders of magnitude higher than that of the CdS cell, and this difference is maintained under illumination as well. The diode factor for the Cd PE cells is also higher. These can be ascribed to the higher interface recombination or to changes in the current transport mechanisms. The CdS deposition affords the growth of a lattice matched window layer, compositional grading at the interface, and passivation of defect states near the interface. The absence of these beneficial effects and the inclusion of a sputter-deposited contact close to the high field region can contribute to a higher  $J_0$  in the Cd PE cells, and hence to a reduction in the  $V_{oc}$  and fill factor. However, the difference in performance between the two is much smaller compared to the case when no Cd treatment is given. The demonstration of ~16% devices by using Cd alone clearly establishes the dominant role of Cd.

In Figs. 5 and 6, we show the spatially resolved line-scans of the micro-PL spectra of a CIGS thin film treated in ammonium hydroxide only and in Cd PE, respectively. The former is the baseline case, and is used as a “surface cleaning step” to remove accumulated alkali impurities. The excitation wavelength is 632.8 nm, and it is strongly absorbed within the first 0.1  $\mu m$  from the surface. The line scans are taken at 1- $\mu m$  intervals over a 50- $\mu m$  length.

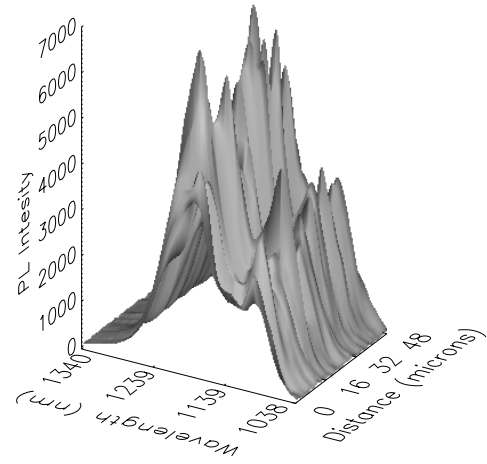


Fig. 5. PL spectra of CIGS thin film treated in  $NH_4OH$ .

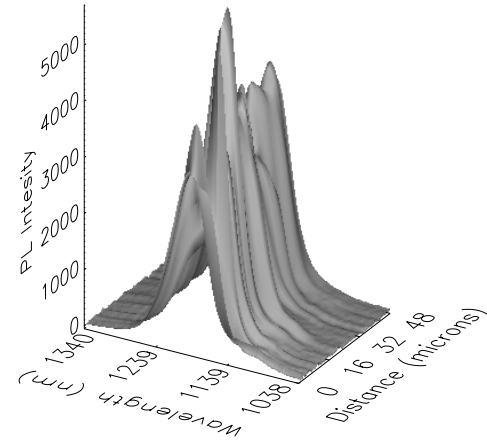


Fig. 6. PL spectra of CIGS thin film treated in Cd PE.

The PL intensities exhibit variation along the length probed, which is attributed to the local variations in composition between the grains and intergrain regions. The spectral dependence shows two broad peaks centered around 1150 nm and 1250 nm for the ammonium hydroxide case. It is well known that the two transitions are donor-to-acceptor pair transitions between shallow energy levels [10]. In the Cd PE sample, the higher energy emission is quenched by the action of Cd. This is likely due to the neutralization of a shallow acceptor-like defect. The filling of Cu vacancies by Cd, or the out-diffusion of Se are the most probable chemical changes that are likely to occur. We can see that changes in the ionization states of shallow levels can lead to a change in the compensation ratio and the conductivity type of the region close to the interface. Similar observations were made in  $CuInSe_2$  single crystals in which the electrical activity of Cd and Zn dopants was closely linked to changes in luminescence, and was associated with a downshift of the peak emission wavelength [11].

In the above, we have shown a series of examples that clearly demonstrate the strong effect of Cd in creating efficient solar cells in CIS alloy thin films prepared by vastly different methods (i.e., co-evaporation and selenization). We attribute this to the ability of Cd and Zn to produce n-type doping or a strong inversion of the surface region. This is most logical explanation for the observed effects. Experimental evidence for this was provided in the studies of Cd and Zn diffusion in  $\text{CuInSe}_2$  single crystals [7,11]. An appreciation of the differences between the single crystal devices and the present day thin film solar cells is essential. However, one must not dismiss the obvious connection. The results shown here suggest that the ability to produce n-type doping could well be at the heart of the CIS alloy thin film solar cells. The evolution of the solar cell can be viewed as a combination of the following three components:

1. Formation of Cd doped, n-type region in the absorber surface region.
2. Compositional mixing and interface grading. Band discontinuities or spikes can be softened by grading. This can minimize the effect of defect states in the interface region and reduce the interface recombination velocity. Shifting the peak of the electric field away from the metallurgical interface can also mitigate the effect of interface recombination. Sulfur can play a useful role in passivating dangling bonds.
3. Wide band gap window layer (CdS) protects the electrical junction from further processing, and facilitates shaping of the electric field within the n-region of the device.

It is clear that the optimal combination of all three components would give rise to an efficient solar cell. Indeed, the same picture can be used to explain the behavior of solar cells made using Zn compounds in CBD, CVD, or ALE environments. The ability to dope CIS alloys n-type, and the inability to do the same in  $\text{CuGaSe}_2$  might offer clues to the differences in their performance.

## CONCLUSIONS

The use of Cd and Zn PE treatments are shown to produce efficient solar cells in CIGS and CIGSS thin film materials. The properties of these cells are compared with those with CdS window layers, and the causes for the differences are identified. We show that the high efficiencies achieved in CBD CdS/CIGS thin film solar cells arise from a set of *key interactions* that could produce n-type doping or inversion, compositional grading, and interface passivation. The results are shown to be applicable to laboratory samples and industrial scale samples from which modules are fabricated. We present a model for the operation of CdS/CIGS devices.

## ACKNOWLEDGMENTS

This work was performed for the Department of Energy under Contract No. DE-AC36-99GO10337 to NREL. We thank D.E. Tarrant of SSI for the supply of samples and his support of this work; J. Dolan for expert technical assistance; T. Moriarty and D. Dunlavy for standardized measurements; R. Bhattacharya, M.A. Contreras, R. Noufi, X. Wu and R. G. Dhere for collaboration; and, J. Benner, and L. Kazmerski for their support.

## REFERENCES

- [1] H.S. Ullal et al., "Polycrystalline Thin Film PV Technologies: From the Laboratory to Commercialization", *Twenty eighth IEEE PVSC*, Anchorage, 2000, pp 301-305.
- [2] D.E. Tarrant and R. R. Gay, "CIS Manufacturing R&D Achievements and Challenges", *Proc. NCPV Program Review Meeting*, 2001, pp. 113-114.
- [3] J. Kessler et al., "Chemical Bath Deposition of CdS on  $\text{CuInSe}_2$ , Etching Effects and Growth Kinetics", *Sixth Int. PVSEC*, New Delhi, 1992, pp 1005-1010.
- [4] C. Heske et al., "Observation of Intermixing at the Buried CdS/ $\text{Cu(In,Ga)Se}_2$  Thin film Solar Cell Heterojunction", *Appl. Phys. Lett.*, 74, 1999, pp 1481-1483.
- [5] K. Ramanathan et al., "High Efficiency Thin Film Solar Cells Without Intermediate Buffer Layers", *Second WCPEC*, Wien, 1998, pp 477-481.
- [6] Y. Hashimoto et al., "Stabilization of Manufacturing Process of CIGS Solar Cell with Treatment of CIGS Surface by In and S Containing Solution", *Jap. J. Appl. Phys.* 39, 2000, pp 415-417.
- [7] P.W. Yu, S.P. Faile, and Y.S. Park, "Cadmium Diffused  $\text{CuInSe}_2$  Junction Diode and Photovoltaic Detection", *Appl. Phys. Lett.* 26, 1975, pp 384-385.
- [8] A.M. Gabor et al., "Band-gap Engineering in  $\text{Cu(In,Ga)Se}_2$  Thin Film Solar Cells Grown From  $(\text{In,Ga})_2\text{Se}_3$  Precursors", *First WCPEC*, Hawaii, 1994, pp 83-86.
- [9] P.K. Johnson et al., "Interface Properties of CIGS(S)/Buffer Layers Formed by the Cd-Partial Electrolyte Process", this Conference.
- [10] S. Zott, K. Leo, M. Ruckh, and H.W. Schock, "Photoluminescence of Polycrystalline  $\text{CuInSe}_2$  Thin Films", *Appl. Phys. Lett.*, 68, 1996, pp. 1144-1146.
- [11] P. Migliorato, J.L. Shay, H.M. Kasper, and S. Wagner, "Analysis of the electrical and luminescent properties of  $\text{CuInSe}_2$ ", *J. Appl. Phys.*, 1975, pp 1777-1782.

<b>REPORT DOCUMENTATION PAGE</b>			Form Approved OMB NO. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.				
1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE May 2002	3. REPORT TYPE AND DATES COVERED 29 <sup>th</sup> IEEE PVSC-Conference Paper May 20-24 2002		
4. TITLE AND SUBTITLE Properties of Cd and Zn Partial Electrolyte Treated CIGS Solar Cells: Preprint		5. FUNDING NUMBERS PVP24301		
6. AUTHOR(S) K. Ramanathan, F.S. Hasoon, S. Smith, A. Mascarenhas, H. Al-Thani, J. Alleman, H.S. Ullal, J. Keane, P.K. Johnson,* and J.R. Sites*				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) National Renewable Energy Laboratory, 1617 Cole Blvd., Golden, CO 80401-3393 *Physics Department, Colorado State University, Fort Collins CO 80523		8. PERFORMING ORGANIZATION REPORT NUMBER		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) National Renewable Energy Laboratory 1617 Cole Blvd. Golden, CO 80401-3393		10. SPONSORING/MONITORING AGENCY REPORT NUMBER  NREL/CP-520-31475		
11. SUPPLEMENTARY NOTES				
12a. DISTRIBUTION/AVAILABILITY STATEMENT National Technical Information Service U.S. Department of Commerce 5285 Port Royal Road Springfield, VA 22161		12b. DISTRIBUTION CODE		
13. ABSTRACT ( <i>Maximum 200 words</i> ): We study the influence of Cd partial baths on the photovoltaic properties of CuInGaSe <sub>2</sub> (CIGS) and CuIn-GaSSe <sub>2</sub> (CIGSS) thin film absorbers. We find that efficient solar cells can be fabricated by this treatment, and we compare their properties with those containing CdS window layers grown by chemical bath deposition. The results suggest that Cd plays a dominant role in establishing efficient photovoltaic junctions in CuInSe <sub>2</sub> alloys. Micron scale photoluminescence scans show non-uniformity along the length probed. Cd treatment quenches one of the luminescence transitions, which indicates a change in shallow acceptor level density. We present a model that helps to explain the evolution of photovoltaic action.				
14. SUBJECT TERMS: PV; CuIn-GaSSe <sub>2</sub> (CIGSS); CuInGaSe <sub>2</sub> (CIGS); thin film absorbers; photoluminescence; chemical bath deposition (CBD); current-voltage; electrolyte; n-type doping; inversion; compositional grading; interface passivation;		15. NUMBER OF PAGES		
		16. PRICE CODE		
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT  UL	